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EVALUATION OF AN OXIDE LAYER ON NI-CR-MO-W ALLOY USING ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY AND SURFACE ANALYSIS TECHNIQUES

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High corrosion resistance under very aggressive conditions is a distinguishing property of Ni-Cr-Mo-W alloys. One such alloy, Alloy 22, is a candidate material for fabrication of the outer layer of high-level nuclear waste (HLNW) packages for the proposed HLNW repository at Yucca Mountain, Nevada, USA.

We are using Electrochemical Impedance Spectroscopy (EIS), ex-situ X-Ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectroscopy (ToF SIMS) to characterize the electrochemical properties and composition of the protective oxide formed on Alloy 22 surfaces. These studies have been conducted at temperatures up to 90°C at potentials from -0.8 V to 0.8 V (vs. Ag/AgCl (sat'd KCl)) in deaerated 5 mol L^{-1} NaCl solution.

Using this combination of techniques, we can correlate the electrical (from EIS) and compositional properties (from XPS, ToF SIMS) of the oxide. At more negative potentials (-0.8 V to -0.4 V) the film exhibits a low charge transfer resistance and high capacitance, indicating the presence of a very defective film with a high concentration of electronic defects. The presence of additional elements in the equivalent circuit, corresponding to water reduction, supports this suggestion. At these potentials, surface analysis techniques show a thin oxide layer with a low concentration of Cr_2O_3. Increasing the potential (to between -0.2 and 0.2 V) leads to a major increase in overall interfacial resistance consistent with the formation of an oxide with a small concentration of electronic defects. At the same time, the surface analysis techniques show increases in the film thickness and the Cr_2O_3 content. A further increase in potential to 0.8 V, in general, leads to a decrease in interfacial resistance throughout the film. When the Cr_2O_3 barrier layer is degraded, then the higher oxidation states of Mo and W species (Mo^{VI}, W^{VI}) increase in concentration and are stored in the outer part of the film (at temperatures up to 60°C). The storage of these high oxidation state ions generates a high interfacial capacitance. At high temperature (above 60°C), the XPS and EIS show that the high oxidation states of Mo and W are absent. We think this is because they dissolve from the oxide under those conditions.

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